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USE OF IONIC MOBILITIES FOR
MEASUREMENTS IN THE LOWER IONOSPHERE

by

George E. Keller

May 1968

U. S. ARMY MATERIEL COMMAND
BALLISTIC RESEARCH LABORATORIES
ABERDEEN PROVING GROUND, MARYLAND

B A L L I S T I C   R E S E A R C H   L A B O R A T O R I E S

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A B E R D E E N   P R O V I N G   G R O U N D, M A R Y L A N D

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ABSTRACT

The results of recent laboratory investigations indicate that
attempts to use ionic mobilities for the identification of positive
ions in the lower ionosphere must necessarily fail. A mobility deter-
mination requires ion-molecule collisions; chemical reactions occurring
during these collisions will cause each mobility spectrum to tend toward
a continuum. Because these reactions do not change the total number
density of ions, conductivity measurements can be made using an average
mobility for ions in air.

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I. INTRODUCTION

Recently, there have been published several suggestions that ionic mobilities be used in lower ionospheric measurements of ion identification and concentration, total ion concentration, and conductivity (Hoult and Kuo, 1967; Hoult and Kuo, 1966; Hoult, 1965; Hale, 1966; Dolezalek, Oster, Coroniti, and Mester, 1966; Dolezalek, 1962). The purpose of this paper is to investigate the effect that ion-molecule reactions will have on the proposed in situ measurements in light of recent laboratory findings.

When ions of a given type drift in a gas under the influence of a static, uniform electric field they lose energy in (elastic) collisions with the gas molecules and gain energy from the electric field between collisions. If the energy acquired by the ions between collisions is small compared with their mean thermal energy, their mean drift velocity, v_d, in the direction of the electric field will be proportional to the field strength, E,

$$v_d = KE. \qquad (1)$$

The constant of proportionality, K, is called the mobility of these ions in the particular gas. If E is increased to the extent that the energy acquired by the ions between collisions becomes larger than their mean thermal energy, K is no longer a constant.

It should be clearly understood that ion-molecule collisions are absolutely essential to the mobility measurement, for without frequent collisions the ions of interest would quickly acquire "field" energies far in excess of their thermal energies.

For ease of comparison, a mobility quoted in the literature is usually a "reduced mobility," K_o, where

$$K_o = K \frac{p}{760} \frac{273}{T}. \qquad (2)$$

Here, p and T are the gas pressure and the temperature, respectively, at which the measurement was performed. Quoted values of reduced

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mobilities usually, but not always, refer to mobilities measured or calculated for the field low enough to insure that K_o has become constant. It can be shown (McDaniel, 1964) that the ratio E/p is the parameter which determines the mean energy that the ions will acquire from the electric field between collisions. Mobilities are usually plotted versus E/p_o, where

$$p_o = p \frac{273}{T},$$ (3)

to take into account the variation of the number density of the gas with respect to temperature. (See McDaniel, 1964, for a more complete discussion of mobility concepts, theories, and measurements.)

II. RESULTS OF LABORATORY MEASUREMENTS

The concept of mobility for ions drifting in a gas and undergoing only elastic collisions has been verified and is well documented. For example, it has been found that the measured drift velocities of noble gas ions (Hornbeck, 1951) and of alkali ions (Tyndall, 1938) drifting in a noble gas under the influence of a weak electric field did indeed approach a constant value as E/p was decreased.

The effect of reactions on mobility measurements first came to light in work on molecular gases. Varney found that in both carbon monoxide and nitrogen (Varney, 1953) the drift velocity versus E/p_o curves had a pronounced, unexpected knee. His nitrogen results are reproduced as Figure 1. He postulated that this unusual behavior was due to reactions between two positive ions in nitrogen, N_2^+ and N_4^+. He suggested that at low values of E/p_o a reaction forming N_4^+ from N_2^+,

$$N_2^+ + N_2 \rightarrow N_4^+,$$ (4)

would dominate so that the drift velocity measured should be that expected for N_4^+ in N_2. Similarly, he suggested that at high values of E/p_o a reaction forming N_2^+ from N_4^+,
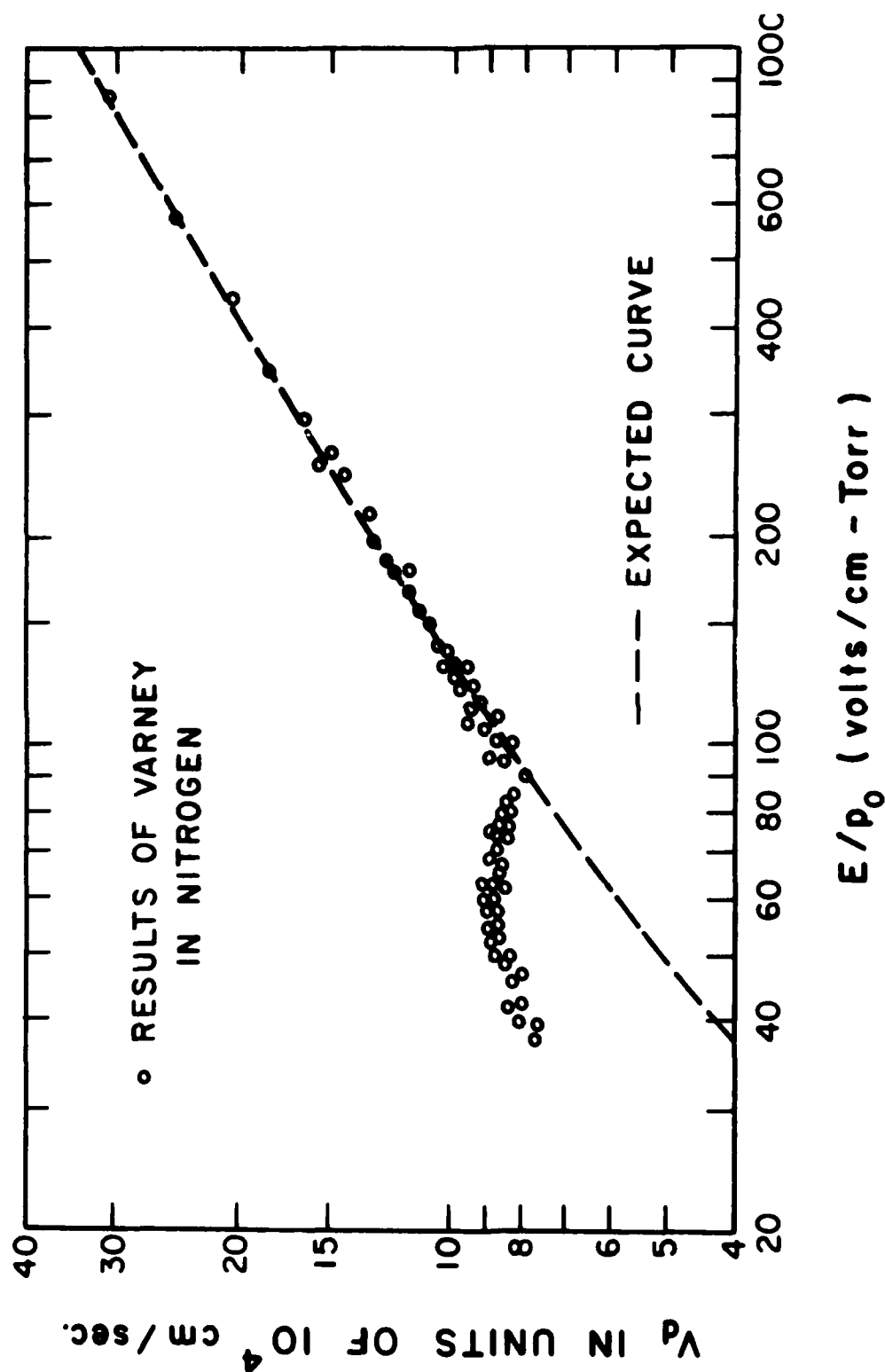
$$N_4^+ + N_2 \rightarrow 2N_2 + N_2^+,$$ (5)

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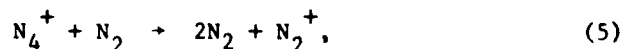
FIGURE 1. RESULTS OF VARNEY IN NITROGEN

would dominate so that the drift velocity measured should be that ex-
pected for N_2^+ in N_2. His apparatus had no mass spectrometer, so he
was unable at that time to verify his ion identification hypothesis.

This identification did seem to be supported by the findings of
Saporoschenko (1958) who later used a mass spectrometer to study the
formation of positive ions in nitrogen. Saporoschenko found that there
were, in fact, four positive ions in nitrogen, N^+, N_2^+, N_3^+, and N_4^+.

Woo (1965) did the latest work on nitrogen with a system lacking a
mass spectrometer for definite ion identification. Even with exhaus-
tive data analysis, he was unable to distinguish all four ions; his
"fast" ion was undoubtedly a composite of N^+ and N_3^+.

In an effort to understand and explain the complications in molecu-
lar gases, several groups have developed mobility devices which incor-
porate mass spectrometric ion identification. The nitrogen results of
one of these groups (Keller, Martin, and McDaniel, 1965) bear careful
consideration.

Keller et al. (1965), using a "drift tube - mass spectrometer,"
found that with some care, and by judicious choice of gas pressure,
drift velocity curves for N^+, N_2^+, and N_4^+ in N_2 could be obtained
which had the expected shape as E/p_0 was changed. However, there were
conditions under which N_2^+ seemed to drift "too fast," and conditions
for which N_4^+ seemed to be "too slow." Under no conditions could the
N_3^+ data be made to display the expected behavior; in particular, the
measured mobility for N_3^+ in N_2 never became constant as E/p_0 was re-
duced. Consideration of the arrival-time spectra of the ions, however,
made it clear that ion-molecule reactions were causing the confusing
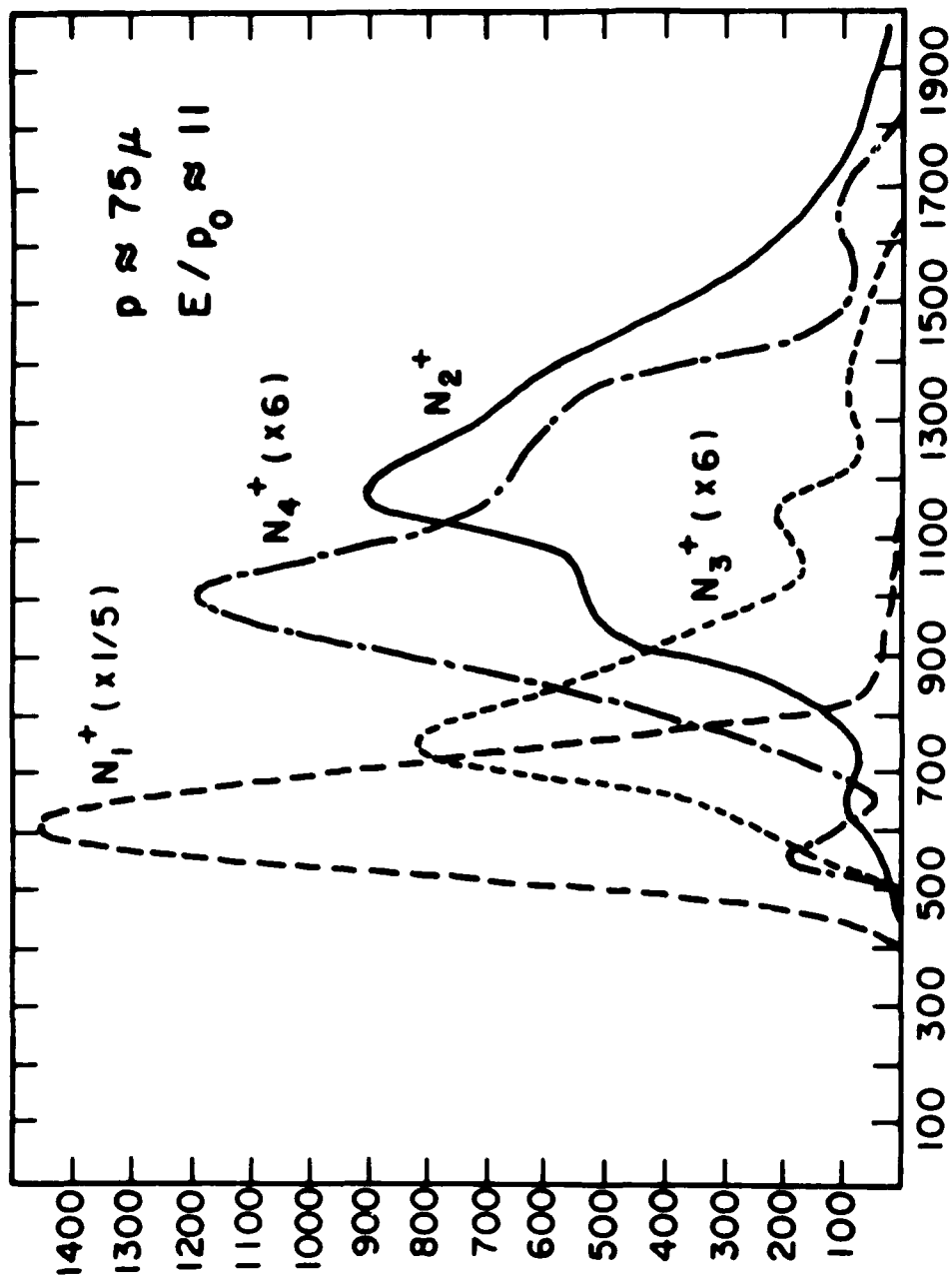results.

Let us consider the method of operation of the drift tube - mass
spectrometer. Ions of the parent gas were formed in a drift tube using
a movable electron bombardment ion source and were caused to drift down
the tube by a weak axial electric field. A small fraction of the ions
which arrived at the end of the drift tube were carried out of a 0.8-mm

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diameter pinhole with the sample gas, passed through an essentially field-free differential pumping chamber into a region of low pressure, where they were sorted by a mass spectrometer and counted individually with an ion multiplier. Ions were created in bursts of only 20 microseconds duration and were sorted into one of twenty counters according to their total time of drift. The raw data for this experiment were in the form of histograms; smoothed data for all four ions in nitrogen are shown in Figure 2.

It is important for the interpretation of arrival time spectra from an experiment of this type to understand that the mass spectrometric sorting assures the assignment of a drift time to an ion whose m/e was known only when it exited the drift tube. Any "history" of ion-molecule reactions undergone in the transit is contained only in the time it took for an ion of the selected m/e to appear. Thus it is not very surprising, when considering arrival time spectra for reacting ions in a gas, to find large areas of overlap in the peaks. In particular, Figure 2 shows N_2^+ and N_4^+ peaks which appear quite similar. The non-symmetrical shapes of each of these curves strongly suggest that ions of each type spent some of their drift time as the other type. The particular field and pressure conditions in use when the data of Figure 2 were taken were those for which the drift velocity of N_4^+ was slower than expected; one then infers that the ions which emerged as N_4^+ ions had spent a significant fraction of their drift time as N_2^+ ions, so that their total drift time would include time as a slower (N_2^+) ion. The ability to unravel completely the information contained in these and similar data would require knowledge of all the reactions and reaction rates for both ions as functions of temperature, pressure, electric field, and excited states.

Conversely, if one reaction taking place in a mobility experiment could be isolated, changes in the peak shapes of the interacting ions could be analyzed to obtain a reaction rate. Just such an analysis has been done by Miller et al. (1967) for ions in hydrogen.

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FIGURE 2. ARRIVAL-TIME SPECTRA IN NITROGEN

DRIFT TIME IN MICROSECONDS

IONS PER CHANNEL PER 40 MINUTES

During a measurement of the drift velocities of the ions in hydrogen using a vastly improved drift tube-mass spectrometer, Albritton et al. (1967) found that while the shape of the H^+ peak in an arrival time spectrum was just what was expected, the H_3^+ peak had a "toe" caused by faster ions. The appropriate arrival time spectra from their investigation are reproduced as Figure 3. Miller et al. (1967) analyzed this toe, and they found that it could be explained by a three-body conversion of H^+ to H_3^+,

$$H^+ + 2H_2 \rightarrow H_3^+ + H_2, \qquad (6)$$
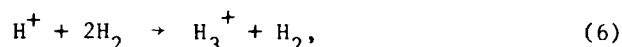
with a reaction rate constant, $k = 3.2(\pm 1.0) \times 10^{-29}$ cm^6/sec. Thus, a reaction rate determination could be made by careful analysis of faster (H^+) ions which were converted to slower (H_3^+) ions in flight.

III. EVALUATION OF RECENT LABORATORY MEASUREMENTS

First, let us consider the drift velocity measurements in nitrogen. Varney's (1953) results suggested and Woo's (1965) results verified that only a tentative understanding of the complications in nitrogen could be accomplished without mass spectrometric identification of the ions. Even with a mass spectrometer, Keller et al. (1965) were prevented from determining a unique "mobility" for N_2^+, N_3^+, and N_4^+ by the reactions taking place. From study of arrival time spectra, they were able to say that there was strong evidence for a pair of strongly pressure-dependent reactions which interconverted N_2^+ and N_4^+ to the extent that one could never be sure that either of these two ions maintained its identity for the entire drift time. The reactions broadened both peaks, the peak for the faster N_4^+ ions toward late times and the peak for the slower N_2^+ ions toward early times.

Second, consider the measurements in hydrogen. Since there was only one appreciable reaction between H^+ and H_3^+ (see Albritton et al., 1967, for details of others), one could deduce from the broadening of the H_3^+ peak that H_3^+ was the end product of the reaction and could proceed to establish the reaction rate. It should be emphasized that
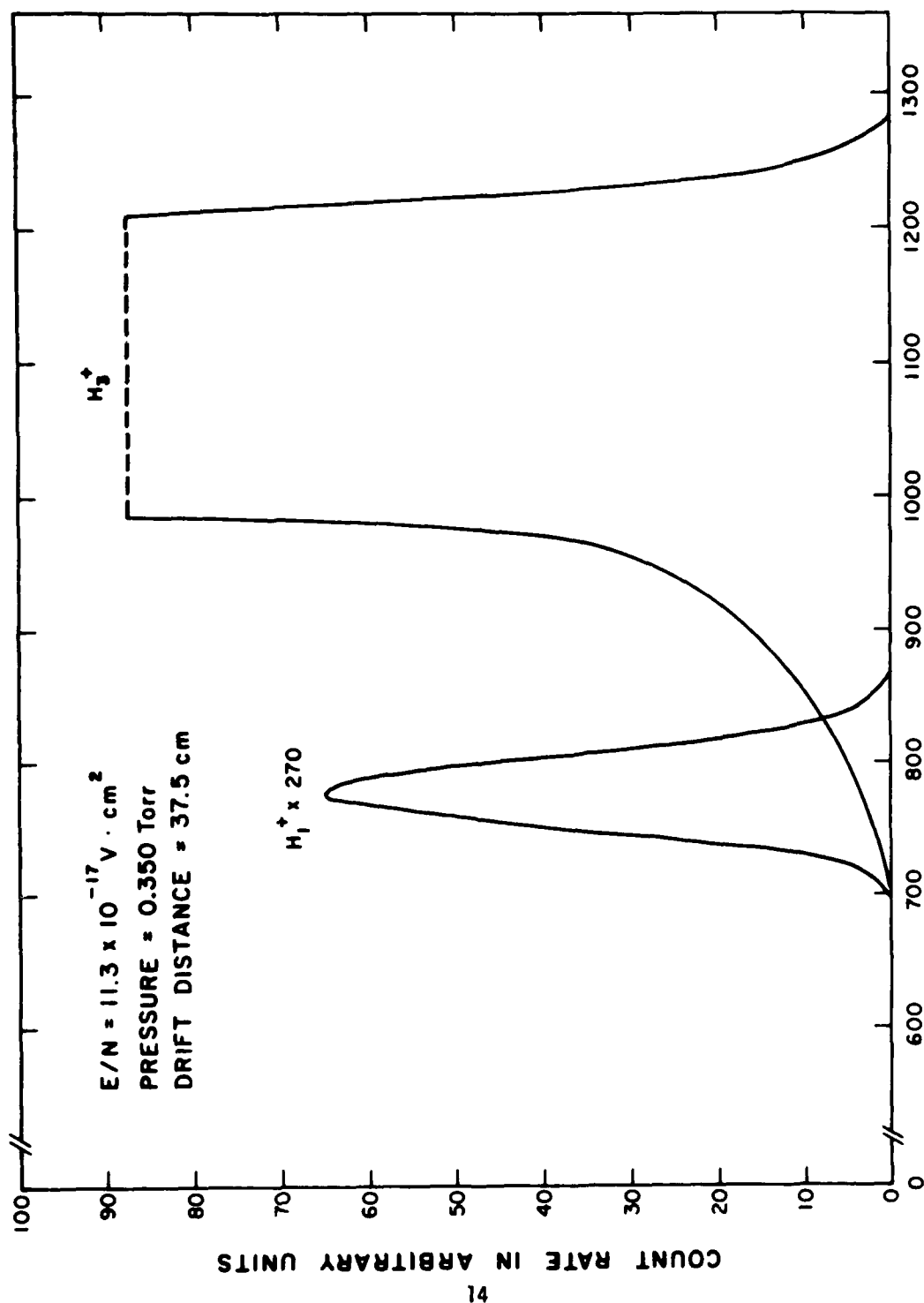
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FIGURE 3. ARRIVAL-TIME SPECTRA IN HYDROGEN

$E/N = 11.3 \times 10^{-17} \, V \cdot cm^2$

PRESSURE = 0.350 Torr

DRIFT DISTANCE = 37.5 cm

H_3^+

$H_1^+ \times 270$

DRIFT TIME IN MICROSECONDS

COUNT RATE IN ARBITRARY UNITS

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without the mass spectrometer the existence of the H^+ could easily have been missed in the presence of the much more intense H_3^+ peak.

Finally, consider what these experiments imply about the expected results of a hypothetical mobility measurement on B^+ ions in B_2 gas. Let us assume that there is a reaction forming B_3^+ ions from B^+,

$$B^+ + 2B_2 \rightarrow B_3^+ + B_2. \tag{7}$$
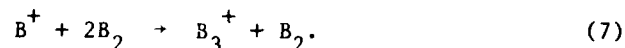
If the reaction rate for (7) is negligible, in the sense that an immeasurably small fraction of the B^+ ions react to form B_3^+ ions under the conditions of the measurement, the only B_3^+ ions which will be seen are those formed by other means. (In hydrogen, for example, H_3^+ is primarily formed from H_2^+ in the source, by the reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$. The reaction rate for this reaction is so large that no H_2^+ ions are ever seen with a drift-tube mass spectrometer; H_3^+ ions created thus can be considered to be primary ions.) Under these conditions, the shape of the B_3^+ peak will be predictable, and it will not be smeared toward, or overlap, the B^+ peak.

If the reaction rate for (7) is appreciable, in the sense that many of the B^+ ions react to form B_3^+, the B_3^+ peak will overlap the B^+ peak, and without the use of a mass spectrometer one could not hope to distinguish between the B^+ ions and the B_3^+ ions formed late in the drift tube.

If the reaction rate for (7) is quite large, in the sense that essentially all the B^+ ions react to form B_3^+ early in the drift tube, the arriving B_3^+ ions cannot be distinguished from B_3^+ otherwise formed in the source, and there is no evidence that B^+ ions had ever existed!

Thus we see that the presence of a nonnegligible reaction in a mobility measurement will cause the arrival time peak of the product ion to be smeared and to overlap that of the reacting ion to the extent that information about the initial concentration of the reacting ion is lost. If there is more than one reaction taking place, the product ion's arrival time spectrum will be complicated by each and every ion from which it is formed during the drift field transit.

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## IV. EFFECT OF LABORATORY FINDINGS ON IN SITU MEASUREMENTS

Let us now consider what effect these laboratory findings will have on measurements in the lower ionosphere which employ ionic mobilities. Since the lower ionosphere is characterized not only by large numbers of ions, electrons, and neutral particles but also by numerous reactions, an effort should be made to evaluate the effect of these reactions on any proposed measurements.

The most intriguing recent suggestion is the use of ionic mobility measurements for number density determinations of individual ionic species. We have seen that reactions could affect the collected currents due to both the number densities of the reacting ions and the number densities of the product ions. The magnitude of the effect of a particular reaction can be most easily measured by comparing the appropriate reaction rate with the collision rate. Gioumousis and Stevenson (1958) give the (ion-molecule) collision rate constant as

$$k_c = 2\pi e (\alpha/\mu)^{\frac{1}{2}}, \tag{8}$$

where e is the electronic charge, α is the polarizability of the gas, and μ is the reduced mass of the colliding particles (for a recent discussion, see Fehsenfeld et al., 1967). This rate constant applies to spiraling or orbiting collisions between thermal energy ions and molecules.

Let us consider two typical atmospheric reactions for which the reaction rates have been measured. The first is

$$N_2^+ + O_2 \rightarrow O_2^+ + N_2, \tag{9}$$
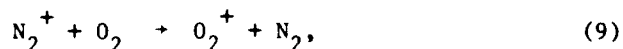
for which the reaction rate has been measured to be $k = 1.0$ (± 0.5) x 10^{-10} cm^3/sec (Ferguson, 1967). For this collision, $k_c = 5.5$ x 10^{-10} cm^3/sec. Thus we see that an original number density of N_2^+ ions will be diminished to less than $1/e$ of its original value after the N_2^+ ions have had an average of six collisions with O_2 molecules. The second reaction to be considered is

$$O_2^+ + NO \rightarrow NO^+ + O_2 \tag{10}$$

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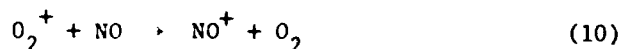
for which the reaction rate constant has been measured to be
$k = 8$ (+2, -5) x 10^{-10} cm^3/sec (Goldan, et al., 1966). For this col-
lision, $k_c = 5.6$ x 10^{-10} cm^3/sec. Thus we see that essentially <u>every</u>
<u>such</u> <u>collision</u> results in a charge transfer! It is not the case that
these reactions have unusually fast reaction rates; rather, a reaction
rate constant of about 10^{-10} cm^3/sec is what one <u>expects</u> for exothermic
charge transfer reactions (Ferguson, 1967).

Therefore, while under the influence of the electric field used
for a mobility measurement, the ions and neutrals will be changing
their identities rapidly due to the collisions imperative for such a
measurement. If the electric field is assumed to be weak, it is true
that the number density of each ion and each neutral will in general be
exactly the same at the collector as it was before the measurement
(in the "free stream"). However, the particles will have lost their
identities; the appropriate reaction rates are such that many identity
changes may take place in a short spatial distance. Thus the drift
time associated with each ion arriving at the collector is not a unique
identifier of the ion type which existed just before entry into the
electric field nor of the ion type which was collected.

While reactions involving positive ions have been used as examples
in the above discussion, the same argument should hold for negative ions.
However, there have been considerably fewer measurements of negative ion
reaction rate constants, so that one cannot as yet be absolutely sure
that there will be enough reactive collisions between negative ions and
neutrals to invalidate mobility measurements in the lower ionosphere.

We can conclude that mobility spectra for a reacting ion-neutral
mixture, of which the atmosphere is one of the worst examples, will be
unable to yield any information about individual positive ion number
densities. Each spectrum can be expected to have the shape of a "humpy
continuum" centered on an average ionic mobility in air.

Thus it is seen that the use of a mobility technique necessitates
collisions. In a reacting gas, such as our ionosphere, these collisions

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lead to reactions which negate the mobility results. Hoping to save
the idea of the experiment, one might suggest elimination of the col-
lisions to stop the reactions. This would only be possible at high
altitudes, however, and would lead to a form of time-of-flight mass
spectrometry, which is far from a mobility measurement.

It has also been suggested that ionic mobilities could be used in
conductivity and/or total ion density measurements in the lower iono-
sphere. Here the reactions will not change the total ion number den-
sity, but they will require that one use a carefully selected average
mobility for ions in air. Thus, with an appreciation for the limited
accuracy necessarily associated with the use of an average mobility
value, ionic mobilities could be used for measurements of conductivity
and/or total ion number densities.

If one assumes that typical atmospheric ions have a mass of about
30 amu, consideration of published mobility data for nitrogen (Keller
et al., 1965; Woo, 1965), oxygen and carbon monoxide (Varney, 1953),
argon (McAfee et al., 1967), and air (Sinnott, et al., 1967) leads one
to estimate an average mobility for positive ions in air of 2.4 ± 1.2
cm^3/V-sec.

V. ACKNOWLEDGMENTS

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13. ABSTRACT

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